Photocatalytic CO_2 reduction by CdS promoted with a zeolitic imidazolate framework

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A B S T R A C T

Metal organic frameworks (MOFs) have emerged as a new class of multifunctional porous materials, and more particularly the family of zeolitic imidazolate frameworks (ZIFs) have shown great promise in the applications of carbon dioxide capture and storage. The CO_2 photoreduction system was established by employing CdS semiconductor and Co-ZIF-9 to act as a catalyst and a cocatalyst, respectively. This hybrid system cooperating with bipyridine and triethanolamine exhibits high catalytic activity in the deoxygenative conversion of CO_2 to CO under visible light irradiation at mild reaction conditions. $^{13}CO_2$ isotopic experiment validated that the produced CO was from the photoreduction of CO_2, instead of organics in the system. The effect of parameters such as cocatalyst concentration, reaction temperature, solvent properties, and water effect were investigated in details. Under the optimized reaction conditions, a high apparent quantum yield of 1.93% was achieved under monochromatic irradiation of 420 nm. The uniqueness of Co-ZIF-9 in supporting CdS for CO_2 reduction reaction was explored by comparing its catalytic functions with other MOFs. *In-situ* photoluminescence and photocurrent generation measurements demonstrated the function of Co-ZIF-9 for promoting electron transfers. At last, a possible reaction mechanism of the photoreduction reaction was proposed.

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1. Introduction

It is now widely accepted that the ever-increasing atmospheric concentration of carbon dioxide mainly caused by the heavy consumption of fossil fuels is the chief contributor to the global warming effect and worldwide climate changes [1,2]. Therefore, there is an urgent need to convert CO_2 into useful substances (*e.g.* CO, CH_4, CH_3OH, HCOOH), which is of significant meanings to environment protection and sustainable development. Among various methods that have been utilized for CO_2 management, the technology of semiconductor-mediated photocatalysis for CO_2 reduction has attracted enormous attentions because it can concurrently reduce the concentration of carbon dioxide and partially relieve the pressure of energy shortage [3–6]. The photocatalytic reduction of CO_2 is typically manipulated by light irradiation under mild conditions of low temperature and atmospheric pressure, and thereby is a more economical, sustainable and environmental-friendly process. However, it remains quite challenge in photocatalytic CO_2 conversion because linear carbon dioxide is the most stable form

of carbon ($\Delta_f G_{298}^0 = -394.36$ kJ/mol) [7], and thus the activation of CO_2 molecule is the key step during its utilization. On the other hand, the high recombination rate of the photogenerated charge carriers on semiconductors during photocatalytic process seriously limits the efficiency of CO_2 photoreduction reaction. Therefore, to effectively realize the crucial mission of CO_2 fixation in the form of chemical fuels using solar energy, appropriate cocatalysts are indispensable in CO_2 conversion systems for promoting the transfer of photoinduced charge carriers and lowering the activation energy for CO_2 conversion reactions, and consequently, accelerating the photocatalytic reaction rate [8–10].

Among the developed catalytic systems for the CO_2 transformations until now, various noble metals (*e.g.* Ru, Ir, Pt, Au, Pd, Ag) are often applied as cocatalysts [11–20]. However, these noble metals are too scarce and thus severely limit the long-term and large-scale developments of these CO_2 conversion systems. So, it still remains challenging but required to develop stable, efficient, and noble-metal-free cocatalyst that can promote the transfer of photogenerated electrons and especially the adsorption/activation of CO_2, for the photochemical reduction of CO_2 by visible light under benign conditions.

In our previous work [21], we have developed a cobalt-containing zeolitic imidazolate framework (termed as Co-ZIF-9) as

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multifunctional cocatalyst that acted as both a redox promoter and a CO_2 absorber/activator for the photochemical splitting of CO_2 into CO under mild conditions. It has been proved that Co-ZIF-9 was stable under the reaction conditions, but the utilization of a Ru-based dye as the light harvester impeded the chemical system for sustainable applications, because the Ru-containing photosensitizer is expensive and unstable after limited catalytic turnovers (TON < 10).

Hence, it is our interest to explore cheap and stable light transducer to cooperate with Co-ZIF-9 to create a hybrid chemical system for the conversion of CO_2 using solar irradiation. Bearing this objective in mind, we concentrated our effort on the semiconductor photocatalysts for searching alternative light sensitizers, and found that cadmium sulphide (CdS) can be a potential candidate to couple with Co-ZIF-9 for establishing a hybrid photochemical system to catalyze CO_2 reduction reactions. CdS semiconductor is one of the well-studied photocatalysts and has been extensively investigated as the visible-light-capturing component in photocatalysis for the conversion of solar energy into chemical energy including CO_2 photoreduction [22–25], water splitting [26–30] and organic photosynthesis [31–34].

In this paper, we report the combination of CdS and Co-ZIF-9, serving as catalyst and cocatalyst, respectively, to cooperatively operate the CO_2-to-CO conversion with visible light under mild reaction conditions (30 °C and 1 atm CO_2). When coupled with bipyridine (bpy) and triethanolamine (TEOA) acting as an assistant electron transfer and an electron donor, the hybrid system effectively reduces CO_2 with a high efficiency, affording an apparent quantum yield of 1.93%. The ^{13}C-labeled isotopic experiment identified the source of the generated CO was derived from the deoxygenative reduction of CO_2. The effects of various parameters such as the cocatalyst concentration, reaction temperature, reaction solvent, and water effect on the catalytic performance were discussed. *In-situ* photoluminescence characterization and photocurrent generation measurements revealed the function of Co-ZIF-9 for promoting electron transfers at CdS photocatalytic system. At last, a possible reaction mechanism of the CO_2 photoreduction system was proposed.

2. Experimental

2.1. Materials, synthesis and characterizations

Chemical reagents used for the synthesis of Co-ZIF-9 sample and the reactions are all purchased from Alfa Aesar, including cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), benzimidazole (H-PhIM), cadmium sulphide (CdS), bipyridine (bpy), triethanolamine (TEOA), *N,N*-dimethylformaide (DMF), dichloromethane (DCM), acetonitrile (MeCN), tetrahydrofuran (THF) and benzotrifluoride (BTF). All the chemicals were used without further purification. Carbon dioxide gas is super grade purity (99.999%) supplied by Fuzhou Lianzhong Industrial Gases Co., Ltd. The $^{13}CO_2$ is 97% enriched. The Co-ZIF-9 sample was synthesized according to the procedure described in the literature with slight modification [35].

Photoluminescence (PL) characterizations were carried out on an Edinburgh FL/FS900 spectrophotometer at room temperature. Photocurrent measurements were performed on a CHI Electrochemical System. Gas chromatographic analysis was carried out on an Agilent 7820A gas chromatography equipped with a thermal conductivity detector (TCD) and a TD-01 packed column. A HP 5973 gas chromatography mass spectrometry (GC–MS) was employed to analyze the products of the $^{13}CO_2$ isotopic experiment and to determine whether other potential products were generated in the liquid phase. Helium used as the carrier gas.

2.2. Catalytic performance

The photocatalytic reactions were carried out in an 80 ml reactor at 1 atm CO_2 partial pressure. Unless otherwise stated, the reaction temperature was controlled at 30 °C by a temperature-controlled circulating water bath. The reaction system contained CdS (20 mg), Co-ZIF-9 (1 mg), bipyridine (10 mg), solvent (5 ml, acetonitrile: H_2O = 3:2) and TEOA (1 ml) and was stirred by a magnetic stirrer. Before illumination, the atmosphere in the reactor was exchanged with high-purity CO_2 gas for several times and then the reactor was tightly closed. A Xe lamp (300 W) with a 420 nm cut-off filter was utilized as the light source and irradiated form the front of the reactor to start the CO_2 reduction reaction. After reactions, the produced gases were analyzed and quantified by Agilent 7820A gas chromatography with respect to calibration curve obtained with different known amount of CO and H_2 (Fig. S1). To ensure the reliability of the results, all the photocatalytic reactions were repeated for twice and the data used in this article were the average value.

2.3. Quantum yield test

For measuring the apparent quantum yield (AQY) of the reaction system, a low-power 420 nm LED lamp (Shenzhen LAMPLIC Science Co. China) was used as the light source. The reactions were conducted on the same photochemical experimental setup under the optimized reaction conditions. A Newport 842-PE Handheld Power/Energy Meter with photodiode detectors was used to measure the intensity of incident monochromatic illumination (24.6 mW/cm^2). The irradiated area for the reaction was controlled at 1.0 cm^2.

2.4. Photocurrent measurement

For photocurrent measurement, the working electrode was made by transferring the powder CdS catalyst into film electrode. The film electrode was obtained by dip-coating catalyst slurry (5 mg/ml in ethanol) onto indium-tin oxide (ITO) glasses that had been cleaned by sonication in chloroform, acetone and ethanol for 30 min, respectively. Then 20 μl of the slurry was spreading onto ITO glass with an exposed area of 0.25 cm^2, and other side parts of the ITO glass were previously covered by Scotch tape. After dried in the air for 24 h, a copper wire was connected to the side part of the ITO glass using conductive tape. Other uncoated parts of the electrode were isolated with epoxy resin. Photocurrent measurements were performed on a CHI Electrochemical System in the mixture of MeCN and H_2O (v/v = 3/2) without any bias potential at room temperature. A graphite rod and an Ag/AgCl (3 M KCl) electrode were used as the counter electrode and reference electrode, respectively. During the measurements, to minimize the influence of the semiconductor layer, the working electrodes were irradiated from the back side.

3. Results and discussion

The catalytic performance of the CdS photocatalyzed CO_2 reduction system was investigated under various reaction conditions, and the results were listed in Table 1. As is shown, by visible light irradiation for 1 h reaction under the reaction conditions, the main products detected form the CdS photocatalytic CO_2 reduction system were CO (50.4 μmol/h) and H_2 (11.1 μmol/h), which is consistent with the observations in our previous work and the literature [8,21]. On the contrary, no CO or H_2 was generated in the dark, saying that this reaction is truly photocatalytic (entry 2, Table 1). Meanwhile, if the CdS semiconductor was removed from the reaction system (entry 3, Table 1), the CO_2 reduction reaction

Table 1
The research of reaction conditions and reference experiments.[a]

Entry	CO (μmol)	H_2 (μmol)	CO + H_2 (μmol)	Sel.$_{CO}$[b] (%)
1	50.4	11.1	61.5	82.0
2[c]	n.d.	n.d.[d]	/	/
3[e]	n.d.	n.d.	/	/
4[f]	n.d.	n.d.	/	/
5[g]	0	2.9	2.9	/
6[h]	0.5	1.6	2.1	23.8
7[i]	40.3	7.5	47.8	84.3
8[j]	n.d.	13.4	13.4	/

[a] Reaction conditions: CdS (20 mg), bipyridine (10 mg), Co-ZIF-9 (4 μmol), solvent (5 ml, MeCN:H_2O = 3:2), TEOA (1 ml), CO_2 (1 atm), $\lambda \geq 420$ nm, 30 °C, 1 h.
[b] Sel.$_{CO}$ = mol CO/mol (H_2 + CO).
[c] In dark.
[d] No detectable.
[e] Without CdS.
[f] Without TEOA.
[g] Without bpy.
[h] Without Co-ZIF-9.
[i] Using physical mixture Co(NO$_3$)$_2$·6H$_2$O and benzimidazole to replace Co-ZIF-9.
[j] Using N_2 instead of CO_2.

Fig. 1. Gas chromatography and mass spectra (m/z = 29) analyses of the carbon source of the generated CO in the photochemical reduction of $^{13}CO_2$.

Fig. 2. Time-production plot of CO and H_2 produced from the Co-ZIF-9 and CdS cocatalyzed CO_2 photoreduction system under visible illumination.
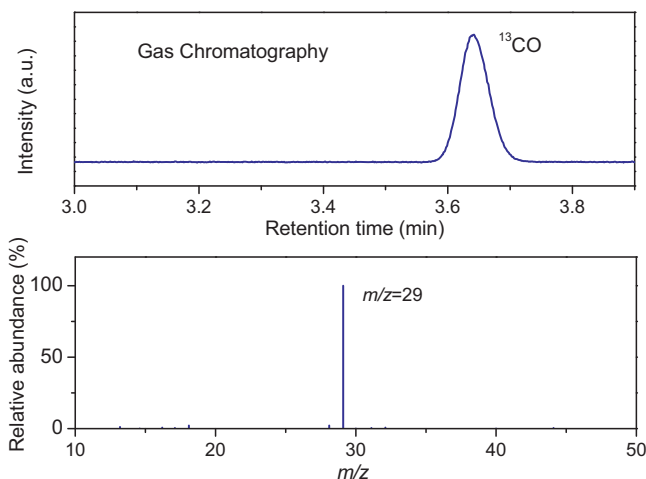
was terminated. These results strongly revealed the necessity of CdS photocatalyst for harnessing visible light to drive the reaction.
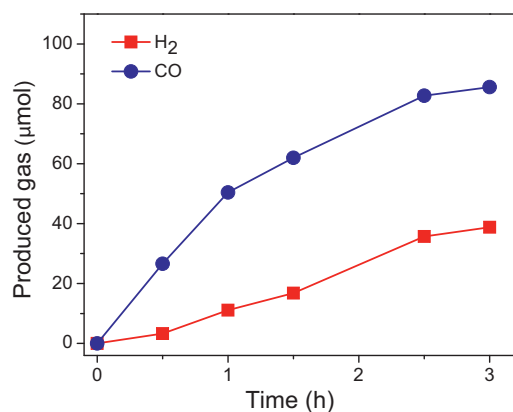
The crucial role of the Co-ZIF-9 cocatalyst on promoting the reduction of CO_2 was demonstrated by the observation that when the Co-ZIF-9 cocatalyst was eliminated from the reaction system, the activity of the catalytic system was dramatically dropped, generating only a few amount of CO and H_2 (entry 6, Table 1). Additionally, the physical mixture of Co-ZIF-9 precursors (Co(NO$_3$)$_2$·6H$_2$O and H-PhIM) was also introduced as cocatalyst for the reaction system to examine their promotional effect for CO_2 photoreduction (entry 7, Table 1). The results showed that the physical mixture of the precursors can cocatalyze the reduction of CO_2 to CO, but with a much lower promotional effect than that of the heterogeneous Co-ZIF-9 cocatalyst. These findings point to the fact that the Co-ZIF-9 cocatalyst can remarkably accelerate the photocatalytic conversion of CO_2 to CO by CdS by acting both as a heterogeneous CO_2 absorber/activator and a redox promoter [21].

In order to validate the involvement of CO_2 in the reaction, we carried out the controlled experiment in high purity N_2 atmosphere (entry 8, Table 1). After 1 h reaction under otherwise identical conditions, only 13.4 μmol H_2 gas was generated, but without any CO production. Comparing with the fact that when the reaction was operated in CO_2 atmosphere (CO production, 50.4 μmol; H_2 production, 11.1 μmol), we can clearly conclude that the photoexcited electrons were favored for the reduction of CO_2 rather than proton in the hybrid reaction system, likely due to the preferable adsorption of CO_2 in the metal–organic framework. This result confirmed that the carbon atom of the produced CO was stemmed from CO_2. To identify the origin of the generated CO, $^{13}CO_2$ was used for the photocatalytic reaction under the same reaction conditions. The produced CO from the isotopic experiment was analyzed by GC–MS. As is shown Fig. 1, after reaction for 1 h, the peak at 3.64 min with the m/z value of 29 in the results of GC–MS analysis was assigned to ^{13}CO. This study provides a powerful proof that the produced CO was absolutely originated from the deoxygenative conversion of CO_2, thus ruling out any doubt on the carbon source of the CO formation. After the reaction, to identify whether other potential products had been generated in liquid phase, the reaction solution was filtrated and the supernatant was analyzed by ion chromatograph, GC–MS and ^{13}C NMR spectroscopy. Results revealed that there was no detectable formic acid, methanol or C—C coupling products formed in the reaction system.

Fig. 2 depicted the evolution of the reaction products generated from the Co-ZIF-9 promoted CO_2 reduction system as a function of reaction time under visible light irradiation. As can be seen, in
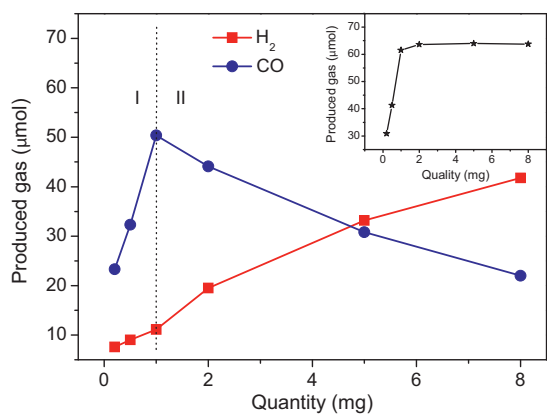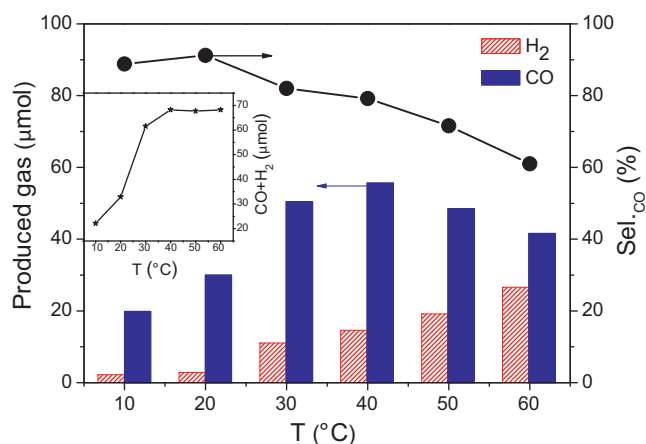
the initial 1 h reaction, the generation of CO (50.4 μmol) and H_2 (8.5 μmol) increased almost linearly with the reaction time. After running the reaction up to 3 h, the accumulated yield of CO and H_2 was increased to 85.6 μmol and 38.8 μmol, respectively, establishing a photocatalytic turnover number (TON, with respect to Co-ZIF-9) greater than 30 for the reaction system. It is evident that after the photocatalytic reaction for 1 h, the generation rate of the products diminished gradually. We attributed this to the intrinsic chemical instability of the CdS semiconductor [36–38] and the depletion/degradation of CO_2 and bpy after long time operations under the reaction conditions, but the Co-ZIF-9 cocatalyst was still stable to preserve its intrinsic catalytic activity, which had been fully confirmed in our previous work [21]. To this end, it is further pursued to develop robust, cost-affordable and environmental friendly candidate as the light sensitizer to cooperate with Co-ZIF-9 for creating a more stable catalytic system for CO_2 photofixation, and the work along this direction is under way in our lab.

Fig. 3 showed the effect of the adding amount of Co-ZIF-9 on the catalytic activity of CdS for CO_2 reduction, which reflected the high cocatalytic efficiency of Co-ZIF-9 and provided us with some insights into the different reaction pathways for the formation of CO and H_2. As shown in the figure, we can clearly find that, even with adding a tiny amount (0.2 mg) of Co-ZIF-9 to the CdS photocatalytic system, the catalytic performance for CO evolution was about 45 times enhanced as compared to the cocatalyst-free system (entry 6, Table 1). The finding thus supported the high promotional ability
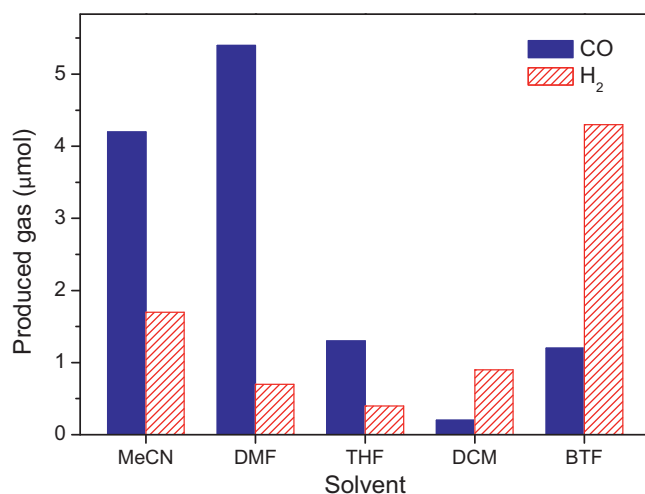
Fig. 3. The effect of the quality of Co-ZIF-9 on the evolution of CO and H_2 generated from the chemical system. Inset is the plot of the total production of products as a function of Co-ZIF-9 amount.

Fig. 4. The generation CO/H_2 and the selectivity of CO formation produced from the Co-ZIF-9 promoted CO_2 conversion system under different reaction temperatures. Inset is the plot of the total generation of the products versus reaction temperature.

Fig. 5. The production of CO and H_2 generated from the CO_2 fixation system using various solvents as the reaction medium.

of the Co-ZIF-9 for CO_2 conversion by CdS photocatalysis, which is consistent with our previous paper [21]. The yield of CO achieved a maximum value of 50.4 μmol when 1 mg Co-ZIF-9 was included in the system. Continuing increase the adding amount of Co-ZIF-9, the production of H_2 increased gradually, but the evolution of CO reduced obviously, which thus disclosed the different reaction pathways for CO and H_2 formations. However, it can be concluded that the adsorption and diffusion of the reactants to the catalytic centers was the main factor that limited the reaction rate when the catalytic system contained the cocatalyst less than 1 mg. While the reaction system involved the cocatalyst more than 1 mg, it is the electron-transfer kinetics that largely determined the reaction rate [21,39]. It was found that the total production of CO and H_2 reached a maximum value when 1 mg Co-ZIF-9 was involved in the catalytic system, and thereafter this value stayed almost unchanged even with additional large amount of Co-ZIF-9 added in the CdS reaction system. This result implied that the electron transfer derived from the photoexcitation of the light sensitizer CdS is identified as the rate-limiting step.

To evaluate the effect of reaction temperature on the catalytic performance of the system, we operated the CO_2 photoreduction reaction at different reaction temperatures. The results revealed that the reaction temperature drastically influenced both the catalytic activity and the CO selectivity of the reaction system. As shown in Fig. 4, in the reaction temperature range of 10–40 °C, the production of CO gradually increased as the reaction temperature
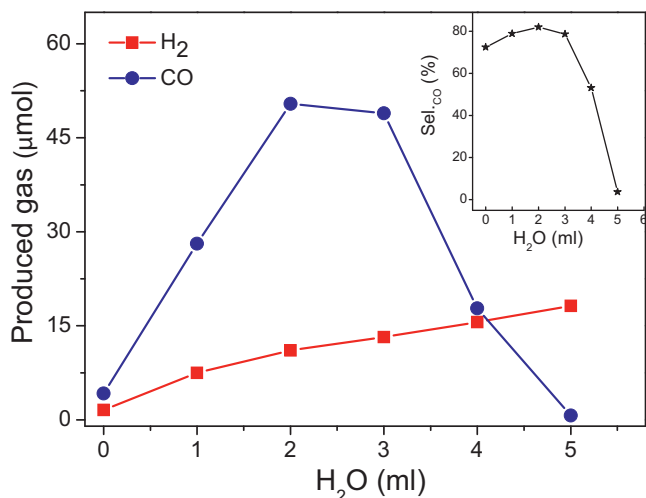
elevated; then, the CO formation was decreased when the temperature was further increased from 40 to 60 °C, and thus achieving a maximum CO yield of 56 μmol for an hour reaction in the system. The reason for the decrease in CO production at relatively high temperature can be ascribed to the liberation/desorption of the reactant CO_2 from the reaction mixture. However, the effect of reaction temperature on H_2 evolution was different from that of CO formation: the yield of H_2 enhanced exclusively along with the reaction temperature increased within the examined temperature region. Due to the different temperature response toward the evolution of CO and H_2, the selectivity of CO formation obtained the highest value of 91.2% at 20 °C. It was also observed that the total production of CO and H_2 increased substantially as the reaction temperature scaled up from 10 °C to 40 °C reaching a maximum value of 68.2 μmol at 40 °C (Fig. 4, Inset). But, the sum of the yields stayed almost unaltered when further increasing the reaction temperature up to 60 °C, which may be regarded as another suggestion that the light-induced electron transfer from the CdS photocatalyst is the rate-determining step. Under the optimal reaction conditions, an apparent quantum yield of 1.93% by monochromatic irradiation at 420 nm was obtained for this CO_2 reduction system by CdS photocatalysis.
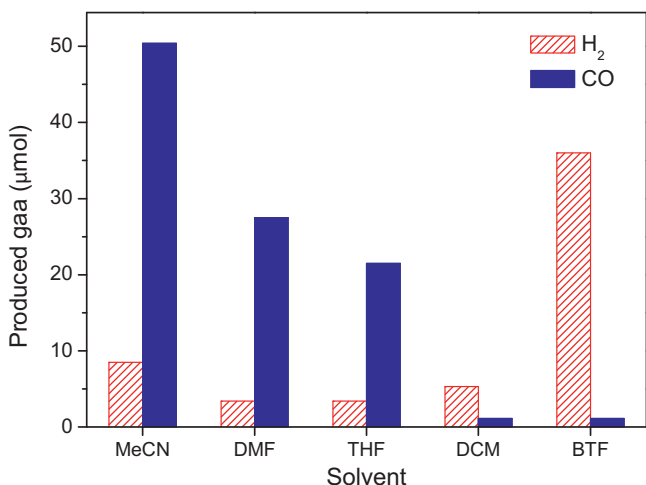
The CO_2 reduction reactions were also performed using various solvents to search for a favorable reaction environment for effectively running CO_2 reduction reaction. Previous literatures [40,41] have documented that solvents containing hybrid atoms (N and/or O) can interact with CO_2 easily through Lewis acid–base interactions and thus will promote the solubilization of CO_2 in the solvents for subsequent reactions, which supports the results of our following experiments. As shown in Fig. 5, when the CO_2 reduction reaction was conducted in the aprotic hybrid-atom-containing solvents such as MeCN, DMF and THF, the reaction was favored to proceed. However, once the catalytic reactions were carried out in DCM and BTF that possess a weak chemical affinity toward CO_2, the system produced only a small amount of CO, but preferred for H_2 production. With the solvents examined under the reaction conditions in our reaction system, the order of catalytic activity for reducing CO_2 into CO formation is DMF > MeCN > THF > BTF > DCM. All the findings demonstrated that selecting appropriate reaction medium is of significant importance for CO_2 conversion.

We also performed the CO_2 photoreduction reactions in water-containing systems and evaluated the effect of adding amount of water on the catalytic performance of the reaction system. Fig. 6 showed that the amount of water contained in the reaction system
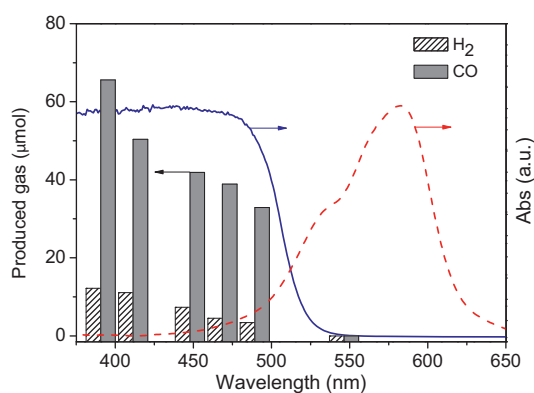
Fig. 6. The production of CO/H$_2$ and the selectivity of CO as a function of water added in the reaction system (the total solvent volume was unchanged). Inset is the plot of CO selectivity versus the adding amount of H$_2$O.

Fig. 7. The generation of CO and H$_2$ evoluted from the reaction system when the reaction medium containing a water ratio of one third.

Fig. 8. The dependence of the wavelength of incident light on the evolution of CO and H$_2$ from the Co-ZIF-9 promoted CO$_2$ photoreduction system. The histogram represents the production of CO and H$_2$. The lines are the UV–vis diffuse reflectance spectrum of CdS (solid) and Co-ZIF-9 (dash).

Table 2
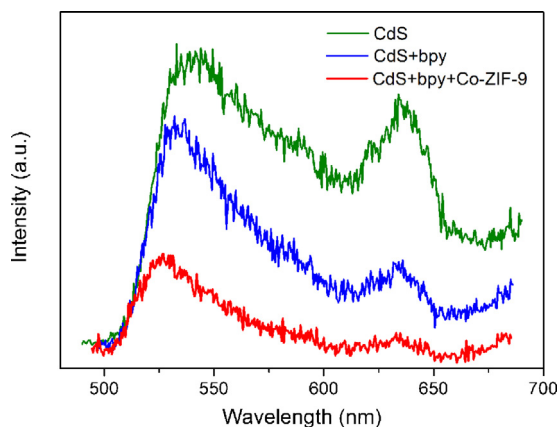Comparison of the cocatalytic function of Co-ZIF-9 with other MOFs.[a]

Entry	CO (μmol)	H$_2$ (μmol)	CO + H$_2$ (μmol)
Co-ZIF-9	50.4	11.1	61.5
Co-MOF-74	39.6	7.7	47.3
Mn-MOF-74	1.0	2.0	3.0
Zn-ZIF-8	0.6	0.6	1.2
Zr-UiO-66-NH$_2$	0.4	0.3	0.7

[a] Reaction conditions are the same as those of Table 1.

has a significant effect on both the activity and CO selectivity. It is obvious that when no water was contained in the reaction medium, the catalytic system can unambiguously catalyze CO$_2$ to CO with a generation rate of 4.2 μmol/h, but the catalytic activity was severely slugged under the reaction conditions. Once 2 ml of water was added to the system, more than 10-fold enhancement in the production of CO was achieved as compared with the water-free system, together with obtaining a selectivity of CO formation with a maximum value of 82%. If the water content was further enlarged, the evolution of CO was gradually reduced. When the reaction was performed using water as the pure reaction medium, the chemical system was almost inactive to operate the CO$_2$-to-CO conversion, but only facilitating H$_2$ evolution, which can be attributed to the poor chemical affinity of water toward CO$_2$ molecules. The remarkable influence of water on the catalytic performance of the CO$_2$ reduction reaction was also observed when using other solvents (DMF, THF, DCM, BTF) as the reaction medium as shown in Fig. 7.

To confirm that the photocatalytic CO$_2$ reduction reaction was really induced by the light excitation of CdS, we conducted the reactions under light irradiation with various wavelengths under the same reaction conditions. Fig. 8 showed the evolution of CO and H$_2$ as a function of the wavelength of the incident light. We

can found that the trend of the production of CO/H$_2$ matches well with the optical adsorption of the CdS semiconductor instead of Co-ZIF-9 cocatalyst. This observation indicated that the photoreduction of CO$_2$ is associated with charge generation, separation and subsequent tandem electron transfer catalysis by the photoexcitation of CdS rather than the Co-ZIF-9 cocatalyst that may exhibit the contribution of metal-to-ligand charge transfer for running the reaction.

The uniqueness of the Co-ZIF-9 cocatalyst for supporting CO$_2$ conversion in the CdS system was demonstrated by comparing the cocatalytic activity with that of some other MOFs under the identical reaction conditions. First, to demonstrate the significance of imidazolate-based ligand confined in Co-ZIF-9 for CO$_2$ reduction in the CdS system, Co-MOF-74 that contains the same metal centers but different organic ligand (2,5-dihydroxyterephthalic acid) was applied as a cocatalyst. Results showed that using Co-MOF-74 as the cocatalyst, the evolution of CO together with H$_2$ was decreased obviously (Table 2). This observation thereby revealed the crucial role of the benzimidazolate ligand for the capture and activation of CO$_2$, originating from the high chemical affinity of imidazolate entities to CO$_2$ and the stabilizing effect of imidazolate motifs on CO$_2^-$ intermediates [42–44]. When employing Mn-MOF-74 as a cocatalyst, there was almost no promotional effect in the production of CO and H$_2$ as compared with the catalyst-free system (entry 6, Table 1), which however strongly reflected that cobalt species are essential for supporting CO$_2$ conversion reaction in our system, due mainly to its excellent mediating ability for redox catalysis [45,46]. Predictably, no obvious CO$_2$ photoreduction catalysis was occurred, when either Zn-ZIF-8 (ligand: 2-methylimidazole) or Zr-UiO-66-NH$_2$ (ligand: NH$_2$-1,4-benzenedicarboxylic acid) was applied as cocatalysts. All these findings strongly underlined the synergetic effect of cobalt and benzimidazolate motifs combined in the harmonious chemical environment of Co-ZIF-9 for promoting CO$_2$ reduction reaction by CdS photoredox catalysis.
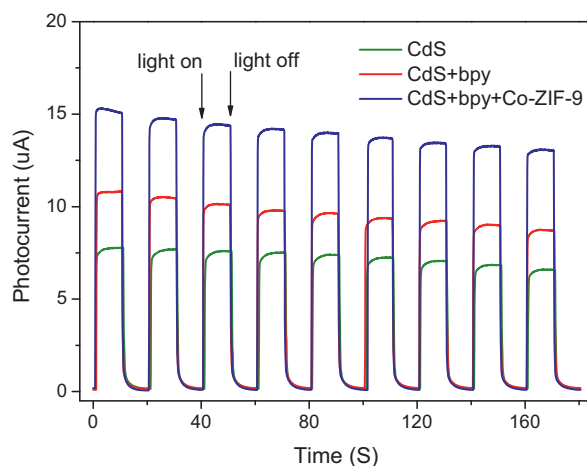
In-situ PL measurement was recorded to demonstrate that the Co-ZIF-9 cocatalyst can effectively suppress the recombination of

Fig. 9. PL spectra of the reaction systems under 400 nm leaser irradiation at room temperature.

Fig. 10. Transient photocurrent response of CO_2 reduction system included different components under visible light irradiations ($\lambda > 420$ nm).

the photo-generated electron–hole pairs in the chemical system. Fig. 9 showed the emission spectra of the CO_2 reduction systems containing different components under excitation at $\lambda = 400$ nm. Two broad-band peaks at *ca.* $\lambda = 530$ and 640 nm were observed in the spectra of the reaction mixture. The former relatively strong emission peak is assigned to the direct recombination of photo-induced electron–hole pairs of CdS, while the emission peak at $\lambda = 640$ nm is attributed to the radiative recombination at deep trap sites derived from lattice imperfection at the surface [47–49]. When bpy was added to the reaction solution, the intensities of the two emissions were diminished obviously, indicating that the quench of the excited electrons was effectively suppressed in the reaction system. Furthermore, once Co-ZIF-9 was added to the system, the intensities of the two emission peaks were further reduced significantly. These observations clearly demonstrated that the Co-ZIF-9 cocatalyst can effectively inhibit the recombination of the light-stimulated charge carries on CdS, leading to the high photocatalytic efficiency, and thus reflecting the superior electron transfer ability of Co-ZIF-9 in the hybrid system.

To further illustrate the function of the Co-ZIF-9 cocatalyst for promoting electron transfer in CdS photocatalytic system, we investigated the photocurrent generation behavior of the system under visible light irradiation. The photocurrent action spectra were showed in Fig. 10. Comparing the experimental results of the systems including the Co-ZIF-9 cocatalyst or not, we can clearly find that when Co-ZIF-9 was added to the system, the photocurrent generation was enhanced remarkably. It is acknowledged that the diffusion of the photoinduced electrons to the back contact and the acceptance of the photogenerated holes by the hole acceptor were the main reasons for photocurrent generation [50]. Therefore, the enhanced photocurrent generation of the system reflected effective transport of light-induced charge carriers, which is also consistent
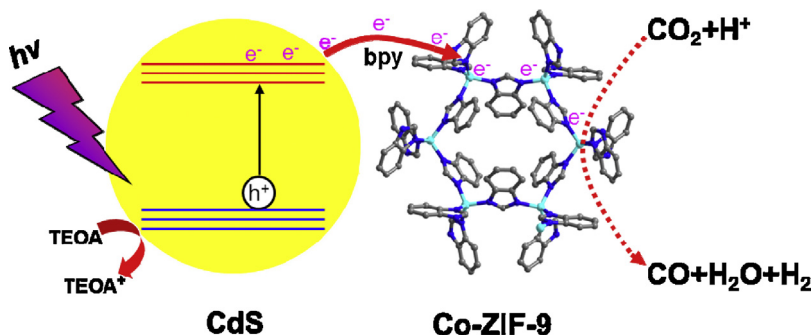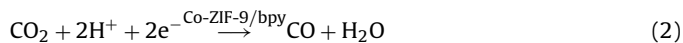
well with the results of the PL measurements. All the observations highlighted the outstanding performance of the Co-ZIF-9 cocatalyst for enhancing charge transfers in the photochemical CO_2 reduction system.

3.1. Possible reaction mechanism

A possible reaction mechanism for the CO_2 photocatalytic reduction system was proposed (Scheme 1). Upon visible light irradiation, the electron–hole pairs were generated on the CdS semiconductor. The visible light-induced electrons (e^-) migrated to the conduction band of CdS and subsequently transferred to interact with CO_2 molecule that adsorbed by Co-ZIF-9 for the reduction of CO_2 to CO, during which the CO_2^- intermediates were formed and stabilized by the benzimidazole linkers defined in Co-ZIF-9 frameworks. At the same time, the protons existed in the reaction system could also be directly reduced by the excited electrons and thus H_2 formed. The holes (h^+) were quenched by TEOA acting as the sacrificial electron donor. The processes can be described briefly as the following equations. Note that triethylamine and ethylenediamine tetra-acetic acid can also act as electron donors in the CO_2 reduction system, but the system containing inorganic electron donors like S^{2-} and SO_3^{2-} are virtually inactive for CO_2 photoreduction.

$$CdS \xrightarrow{h\nu} e^-(CdS) + h^+(CdS) \tag{1}$$

$$CO_2 + 2H^+ + 2e^- \xrightarrow{Co\text{-}ZIF\text{-}9/bpy} CO + H_2O \tag{2}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{3}$$

$$TEOA + h^+ \rightarrow TEOA^+ \tag{4}$$

Scheme 1. Possible reaction mechanism for the Co-ZIF-9 cocatalyzed photoreduction of CO_2 employing CdS as the light harvester.

4. Conclusions

A noble-metal-free photocatalytic CO_2 reduction system was established by utilizing the cobalt-containing zeolitic imidazolate framework Co-ZIF-9 as a cocatalyst coupled with CdS semiconductor as the light harvester under benign reaction conditions. $^{13}CO_2$ isotropic experiments identified that the carbon source of the produced CO was CO_2. Various reaction conditions were investigated to operate effective CO_2 conversions, and under the optimal conditions, as apparent quantum yield of 1.93% was achieved for the photochemical system. *In-situ* PL measurements and the photocurrent generation revealed the function of Co-ZIF-9 for promoting electron transfers in the CdS photocatalytic system. We believed that the work presented here will bring new opportunities in CO_2 photoconversion by merging the merits of metal–organic cocatalysts and semiconductor light harvesters.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2014.07.026.

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